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# PATENT SPECIFICATION

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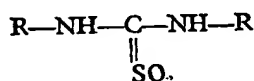


## (54) IMPROVEMENTS IN OR RELATING TO DYEING HUMAN HAIR

(71) We, THERACHEMIE CHEMISCH THERAPEUTISCHE GESELLSCHAFT MBH, a German Company, of 44 Berliner Allee, Duesseldorf 4000, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the dyeing of human hair.

More particularly the invention relates to processes and agents for dyeing human hair by means of oxidation dyes which contain as an additive a composition comprising a thiocarbamide derivative of the formula:—

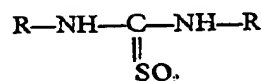


wherein R represents hydrogen or an alkyl radical having 1 to 4 carbon atoms, a reducing agent and an organic chelating agent.

Oxidation dyes are used to a considerable extent for the purpose of dyeing human hair. Reducing agents are generally added in a smaller quantity to the oxidation dyes in order to avoid oxidation of the dyes during storage and before mixing with an oxidizing agent. However, these additives are insufficient to prevent oxidation of the dye in the mixing container after adding H<sub>2</sub>O<sub>2</sub> and before or during application of the dye solution or cream to the hair. This reduces the colouring power of the mixture and renders it extremely difficult to obtain uniform colouration of the hair. Increasing the content of reducing agent in the dyeing cream does not provide a remedy, since, as a result of reduction, a corresponding portion of the required oxidizing agent which has been added is rendered ineffective.

It has now been discovered that these disadvantages can be substantially avoided by using the process, described hereinafter, for dyeing human hair with oxidation dyes and, if

required, with additives known for hair-dyeing agents. Accordingly the present invention provides a process for dyeing human hair characterised in that the hair is treated at a temperature of from 10 to 40°C with a composition in the form of a solution, emulsion or cream which composition comprises a thiocarbamide derivative of the formula:



wherein R represents hydrogen or an alkyl radical having 1 to 4 carbon atoms, a reducing agent and an organic chelating agent.

Suitable thiocarbamide derivatives are compounds such as N,N' - dimethylthiocarbamide dioxide, N,N' - diethylthiocarbamide dioxide, N,N' - dipropylthiocarbamide dioxide and N,N' - dibutylthiocarbamide dioxide, and N - methylthiocarbamide dioxide, N - ethylthiocarbamide dioxide, N - propylthiocarbamide dioxide and N - butylthiocarbamide dioxide. Preferably, thiocarbamide dioxide is used. Alternatively, mixtures of the said compounds may be used if desired.

The reducing agents used are compounds known for this purpose, such as sodium sulphite, thioglycolic acid or ascorbic acid. Alternatively, water-soluble salts of these compounds, such as the sodium, potassium, ammonium or ethanolamine salts may be used instead of the free acids. Suitable organic chelating agents are: hydroxyalkanediphosphonic acids such as 1 - hydroxyethane - 1, 1 - diphosphonic acid and 1 - hydroxypropane - 1, 1 - diphosphonic acid, aminoalkanediphosphonic acids such as 1 - aminoethane - 1, 1 - diphosphonic acid and 1 - aminopropane - 1, 1 - diphosphonic acid, aminotriethylenephosphonic acid, 8 - hydroxyquinoline, nitrilotriacetic acid, diethylenetriaminepentaacetic acid and preferably ethylenediaminetetraacetic acid. Alternatively, water-soluble salts of these acids such as the sodium,

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potassium, ammonium or ethanolamine salts may be used instead of the acids.

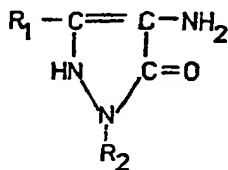
The reducing agent is added in quantities of from 0.1 to 3, preferably 1 to 2, percent by weight related to the total composition, the organic chelating agents in quantities of from 0.1 to 2, preferably 0.1 to 0.5, percent by weight related to the total composition and thiocarbamide derivative in quantities of from 0.05 to 2, preferably 0.1 to 0.5, percent by weight related to the total composition.

The oxidation dyes used are preferably the aromatic diamines, phenols and/or aminophenols known for this purpose. The oxidation dyes comprise two components; a coupling component and a developer component. Particularly suitable developer components are substituted ortho- and para- phenylenediamines, N-alkylaminoanilines, N,N-dialkylaminoanilines and aminophenols such as

p - toluylenediamine  
o - toluylenediamine  
2,5 - diaminoanisole  
p - aminodiphenylamine  
N,N - dimethylaminoaniline  
N,N - diethylaminoaniline  
N - methylaminoaniline  
N - ethylaminoaniline and  
N,N -  $\beta$  - hydroxyethylaminoaniline.

Aromatic diamines, phenols and aminophenols in which, in particular, a functional group such as a hydroxyl-, amino- or alkoxy group is in the meta position relative to the amino- or hydroxyl group, may also be used as a coupling component. Suitable compounds are, for example, resorcinol, m - toluylenediamine, 2,4 - diaminoanisole, m - aminophenol, m - methylaminophenol and  $\alpha$  - naphthol.

Pyrazolone derivatives, such as are described in U.K. Patent Specification No. 1,213,697, may also be used as components for the oxidation dyes. The latter specification proposes 4 - aminopyrazolones of the general formula:—



as a developer component, wherein  $R_1$  and  $R_2$  each represent a hydrogen atom or an organic radical having 1 to 10 carbon atoms.

The organic radical  $R_1$  of the 4 - aminopyrazolone may, for example, comprise an alkyl radical having 1 to 10 carbon atoms,

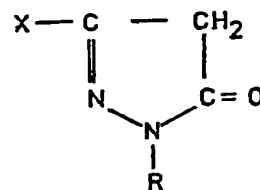
or an aryl or heterocyclic radical. Furthermore, functional groups such as  $-OH$ ,  $-NH_2$ ,  $-NHCH_3$ ,  $-N(CH_3)_2$  or halogen atoms, particularly chlorine, may also be present. The groups  $-COOH$ ,  $-COOR'$ ,  $-CONHR'$   $-CONR'R''$  may be present as organic radicals, wherein  $R'$  and  $R''$  represent a lower alkyl or hydroxyalkyl radical having 1 to 4 carbon atoms.

The organic radical  $R_2$  of the 4 - aminopyrazolone may comprise an alkyl radical having 1 to 10 carbon atoms or, alternately, an aryl or heterocyclic radical. Furthermore, functional groups may also be present. Hydrocarbon radicals which have 1 to 10 carbon atoms, and which contain  $-OH$ ,  $-NH_2$ ,  $-COOH$ ,  $-CONH_2$ ,  $-SO_3H$  and  $-SO_2NH_2$  as functional groups, are particularly suitable.

A phenyl radical is particularly suitable as the aryl radical. The phenyl radical may contain alkyl or hydroxyalkyl groups having 1 to 4 carbon atoms or other substituents such as  $NH_2$ ,  $OH$ ,  $COOH$ ,  $CONH_2$ ,  $SO_3H$  and  $SO_2NH_2$  group.

It is frequently advantageous to use the 4 - aminopyrazolones in the form of their salts, preferably the hydrochloride salts, since this reduces their sensitivity to air.

3 - aminopyrazolones of the general formula:



are also suitable as the coupling component, wherein  $R$  represents a hydrogen atom, an alkyl or phenyl radical and  $X$  represents an  $NH_2$ -,  $NHR$ -,  $NR_1R_2$  group ( $R_1$  and  $R_2$  being alkyl radicals having 1 to 4 carbon atoms) or an  $OH$  group.

When using these oxidation dyes, the colouring of the hair is substantially intensified by the addition of thiocarbamide dioxide in combination with a reducing agent and an organic chelating agent.

Likewise, the 4 - aminopyrazolones mentioned as developer components may be combined with the aromatic diamines, phenols or aminophenols already mentioned above as coupling components.

The concentration of the dyes or dye components is dependent to a certain extent upon the intended use, particularly upon the degree of the desired colouration. The concentration is usually from 0.1 to 5 percent by weight, preferably 0.5 to 2 percent by weight, related to the total composition.

When using oxidation dyes, the colours are developed by atmospheric oxygen, or, preferably, by chemical oxidizing agents. Preferably, hydrogen peroxide or its products of addition, such as percarbamide, melamineperhydrate, or sodium perborate, are used as chemical oxidizing agents.

The hair is dyed at a temperature of from 10 to 40°C, but preferably at a temperature within the range 15 to 25°C. The hair dyes may be used in the form of aqueous solutions, or especially in the form of creams or emulsions. For this purpose, the dyes or dye components may be mixed with wetting agents or washing agents, particularly anionic or nonionic. Alkylbenzene sulphonates, fatty alcohol sulphates, alkyl sulphonates, fatty acid ethanalamides, products of addition of ethylene oxide to fatty acids and fatty alcohols, and fatty alcohol ether sulphates, are particularly suitable as wetting and washing agents. The hair dyes may also be manufactured in the form of shampoos, particularly cream-like shampoos.

Other known additives which may be present are thickeners such as methyl cellulose, starch, higher fatty alcohols, Vaseline (Registered Trade Mark), paraffin oil, and fatty acids, as well as perfume oil or hair lotion such as pantothenic acid or cholesterol.

The additives are used in the conventional quantities used for these purposes. Suitable quantities of the wetting agent additive are particularly from 0.5 to 30 percent by weight related to the total composition, and suitable quantities of the thickener additives are particularly from 0.1 to 25 percent by weight related to the total composition.

The pH-value of the hair dyes may lie in the conventional slightly acid to alkaline range. Preferably, the hair dyes are adjusted to a pH-value of from 8 to 10.

By virtue of the process according to the invention, and by employing the novel hair dyes, it is possible, to a considerable extent, to prevent oxidation of the oxidation dyes, based on diamines, phenols or aminophenols, in the mixing container after adding the oxidizing agent, either before or during application of the dye solution to the hair. The colouring power of the mixture is thus maintained and it is possible to obtain uniform colouring of the hair. In this manner, the hair can be coloured in considerably darker tints with light-coloured dyeing creams. In so far as oxidation dyes based on pyrazole derivatives are used, the novel process effects more intensive dyeing of the hair.

The invention will be illustrated with reference to the following Examples.

#### Example 1

1.75 Parts by weight of resorcinol, 1.6 parts by weight of p - toluylenediamine, 0.45 parts by weight of m - diaminoanisole, 0.38

parts by weight of naphthol and 3 parts by weight of 1,2 - propylene glycol were dissolved in 30 parts by weight of water. 0.1 Parts by weight of thiocarbamide dioxide, 0.9 parts by weight of thioglycollic acid and 2 parts by weight of ethylenediaminetetraacetic acid were also added. The mixture thus obtained was incorporated in 50 parts by weight of an emulsion containing 10 parts by weight of fatty alcohol (carbon chain length  $C_{16}-C_{18}$ ), 26 parts by weight of sodium lauryl ethersulphate and 34 parts by weight of water. The pH-value was adjusted to 9.5 by means of ammonia, and the emulsion was made up to 100 parts by weight with water.

50G of 9% hydrogen peroxide were added to 50 g of this light-beige coloured cream, thoroughly stirred, and applied to strands of grey hair which had not been pre-treated. During the entire period of application of about 30 minutes, the cream retains a light colour which gradually changes to a light grey tint, whereas the hair is dyed jet-black.

The above-described procedure was repeated for the purpose of comparison, but with the difference that the cream used did not an additive of thiocarbamide dioxide, thioglycollic acid and ethylenediaminetetraacetic acid. Immediately after the hydrogen peroxide solution was added, this cream exhibited a dark grey colour which rapidly became more intense.

When as described above, one of the said additives, i.e. thiocarbamide dioxide or thioglycollic acid or ethylenediaminetetraacetic acid, was omitted in the cream used, and the same procedure was followed, the creams darkened to a deep black by way of grey within a few minutes after adding the hydrogen peroxide solution.

#### Example 2

A cream as described in Example 1, paragraph 1, was prepared, except that the thioglycollic acid was replaced by 1 part by weight of sodium sulphite.

50G of 9% hydrogen peroxide was added to 50 g of this light-coloured cream, and the cream was applied to grey strands of hair after mixing. The period of treatment was about 25 minutes at a temperature of 28°C. The cream assumes only a light grey tint during treatment, while the hair is dyed jet-black.

#### Example 3

A cream as described in Example 1, paragraph 1, was prepared, except that 1.5 parts by weight of 8 - hydroxyquinoline were added instead of the ethylenediaminetetraacetic acid.

50 G of 9% hydrogen peroxide were added to 50 g of the light-coloured cream thus obtained, and strands of grey hair were treated therewith for 25 minutes at 28°C. The colour of the dyeing cream changed only

slightly during the entire period of application, while the hair was dyed black.

#### Example 4

A dyeing cream as described in Example 1, paragraph 1, was prepared, except that 1 part by weight of sodium sulphite was added instead of the thioglycollic acid, and 1.5 parts by weight of 1 - hydroxyethane - 1,1 - diphosphonic acid were added instead of the ethylenediaminetetraacetic acid.

50 G of the light-coloured cream thus obtained were mixed with 50 g of 9% hydrogen peroxide solution and applied to strands of grey hair which had not been pre-treated. The period of treatment was about 30 minutes at about 30°C. The hair was dyed jet-black after this period of time, while the dyeing cream had assumed only a light grey colour.

Comparable results were obtained if, in a modification of the procedures according to Examples 1 to 4, an equivalent quantity of aromatic diamines, phenols or aminophenols of the kind given in the foregoing specification were used as developer components and coupling components. The development of colour in the cream is inhibited to a considerable extent in all cases.

#### Example 5

A dyeing cream was prepared as in Example 1, paragraph 1, except that 1 part by weight of 1 - phenyl - 3 - carbamoyl - 4 - aminopyrazolone - 5 and 0.9 parts by weight of 1 - phenyl - 3 - methylpyrazolone - 5 were used as dye components.

50 G of this cream were mixed with 50 g of 9%  $H_2O_2$ , and grey hair was treated therewith for 25 minutes at room temperature. A deep violet colour was obtained. When the hair was treated in a similar manner, but with a dyeing cream which contained no thioglycollic acid, thiocarbamide dioxide or ethylenediaminetetraacetic acid, individually or mixed, only lilac colours were obtained whose intensity was considerably less.

Comparable results were obtained when, in a modification of the procedure described above, an equivalent quantity of 4 - aminopyrazolones or 3 - aminopyrazolones of the kind stated in the specification were used as developer and coupling components.

#### Example 6

A composition was prepared by dissolving

0.85 parts by weight of p - toluylenediamine sulphate  
0.25 parts by weight of p - aminophenol hydrochloride  
0.08 parts by weight of resorcinol and  
0.1 parts by weight of m - aminophenol  
in 20 parts by weight of water to which ammonia was added. 0.1 Parts by weight of

$N,N'$  - dimethylthiocarbamide dioxide, 1.5 parts by weight of ascorbic acid and 2 parts by weight of ethylenediaminetetraacetic acid were also added.

The mixture thus obtained was incorporated in 50 parts by weight of an emulsion containing 10 parts by weight of fatty alcohol (carbon chain length  $C_{16}$  to  $C_{18}$ ), 26 parts by weight of sodium lauryl ether sulphate and 34 parts by weight of water. The pH-value was adjusted to 9.5 with ammonia and the mixture was made up to 100 parts by weight with water. 50 G of 6% hydrogen peroxide were added to 50 g of this almost white-coloured dyeing cream, which was then well stirred, and the cream was applied to dark-blond hair. The reaction time was about 10 minutes. The hair was tinted a light brown. The dyeing cream changed colour to only a slight extent within the stated time.

Virtually the same results were obtained when, in a modification of the procedure described above  $N,N'$  - diethylthiocarbamide dioxide,  $N,N'$  - dipropylthiocarbamide dioxide or  $N,N'$  - dibutylthiocarbamide dioxide were used as the thiocarbamide derivative.

The above-described procedure was repeated for the purpose of comparison, but with the difference that the cream used contained no  $N,N'$  - dimethylthiocarbamide dioxide, ascorbic acid or ethylenediaminetetraacetic acid. This cream exhibited a brownish colour immediately after adding the hydrogen peroxide solution.

#### Example 7

0.001 Mol 1 - phenyl - 3 - dimethylamide - 4 - aminopyrazolone - (5)

0.001 mol  $\alpha$  - naphthol

were dissolved in 20 parts by weight of water to which ammonia was added. 0.1 Parts by weight of N - methylthiocarbamide dioxide, 1 part by weight of sodium sulphite, and 0.2 parts by weight of diethylenetriaminepentaacetic acid were also added.

The mixture thus obtained was incorporated in 50 parts by weight of an emulsion containing 10 parts by weight of fatty alcohol (carbon chain length ( $C_{16}$  to  $C_{18}$ ), 26 parts by weight of sodium lauryl ether sulphate, and 34 parts by weight of water. The pH-value was adjusted to 9.5 with ammonia and the mixture was made up to 100 parts by weight with water. 50 G of 6% hydrogen peroxide were added to 50 g of this almost white-coloured dyeing cream, which was then well stirred, and the cream was applied to white hair. The reaction period was about 10 minutes. The hair was dyed an intense blue color.

Virtually the same results were obtained when in a modification of the procedure according to paragraphs 1 and 2, N - ethylthiocarbamide dioxide, N - propylthiocarb-

amide dioxide or N - butylthiocarbamide dioxide was used as the thiocarbamide derivative.

5 The above-described procedure was repeated for the purpose of comparison, but with the difference that the cream used contained no N - methylthiocarbamide dioxide, sodium sulphite or diethylenetriaminepenta-  
10 acetic acid. The colour obtained on the white hair was only slightly blue.

#### Example 8

15 Dyeing creams as described in Example 1, paragraphs 1 and 2, were prepared, except that a corresponding quantity of the sodium, potassium, ammonium and ethanolamine salt was used instead of the thioglycollic acid in each case. The same results were obtained as with the thioglycollic acid.

#### Example 9

20 Dyeing creams as described in Example 6, paragraphs 1 and 2, were prepared, except that a corresponding quantity of the sodium, potassium, ammonium and ethanolamine salt was used instead of the ascorbic acid in each case. The same results were obtained as with ascorbic acid.

#### Example 10

30 Dyeing creams as described in Example 1, paragraphs 1 and 2, were prepared, except that a corresponding quantity of 1 - hydroxyethane - 1, 1 - diphosphonic acid, 1 - hydroxypropane - 1, 1 - diphosphonic acid, 1 - aminoethane - 1, 1 - diphosphonic acid, 1 - aminopropane - 1, 1 - diphosphonic acid, 35 aminotrimethylene - phosphonic acid and nitrilotriacetic acid was used instead of ethylenediaminetetraacetic acid as complexing agents.

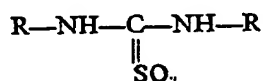
40 When dyeing the hair, virtually the same results were obtained as with ethylenediaminetetraacetic acid.

#### Example 11

45 The organic chelating agents present in the form of the free acids in Examples 1 to 10 were replaced by the corresponding sodium, potassium, ammonium and ethanolamine salts. The same results were obtained as with the acids.

#### WHAT WE CLAIM IS:—

50 1. A process for dyeing human hair with oxidation dyes, and, if required, with additives known for hair-dyes, which comprises treating the hair at a temperature of from 10 to 40°C with a composition in the form of a solution, emulsion or cream the composition comprising a thiocarbamide derivative of the formula



wherein R represents hydrogen or an alkyl radical having 1 to 4 carbon atoms, a reducing agent and an organic chelating agent. 60

2. A process as claimed in claim 1 in which the thiocarbamide derivative is thiocarbamide dioxide.

3. A process as claimed in claim 2, in which the reducing agent is thioglycollic acid or a water-soluble salt thereof. 65

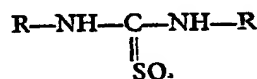
4. A process as claimed in claim 2 or 3 in which the organic chelating agent is ethylenediaminetetraacetic acid, or a water-soluble salt thereof. 70

5. A process as claimed in claim 1, in which the thiocarbamide derivative is an N - alkylthiocarbamide dioxide or N,N' - dialkylthiocarbamide dioxide. 75

6. A process as claimed in claim 5, in which the reducing agent is thioglycollic acid, or a water-soluble salt thereof.

7. A process as claimed in claim 5 or 6, in which the organic chelating agent is ethylenediamine - tetraacetic acid, or a water-soluble salt thereof. 80

8. A composition for dyeing human hair, containing oxidation dyes and, if required, other additives known for hair-dyes, which comprises a thiocarbamide derivative of the formula 85



wherein R represents hydrogen or an alkyl radical having 1 to 4 carbon atoms, in quantities of from 0.05 to 2 percent by weight and an organic chelating agent in quantities of from 0.1 to 2 percent by weight and a reducing agent in quantities of from 0.1 to 3 percent by weight of the total composition. 95

9. A composition as claimed in claim 8, in which the thiocarbamide derivative is thiocarbamide dioxide.

10. A composition as claimed in claim 9, in which the reducing agent is thioglycollic acid. 100

11. A composition as claimed in claim 9 or 10, in which the organic chelating agent is ethylenediaminetetraacetic acid.

12. A composition as claimed in claim 8, in which the thiocarbamide derivative is an N - alkylthiocarbamide dioxide or N,N' - dialkylthiocarbamide dioxide. 105

13. A composition as claimed in claim 12, in which the reducing agent is thioglycollic acid. 110

14. A composition as claimed in claim 12 or 13 in which the organic chelating agent is ethylenediaminetetraacetic acid.

15. A composition as claimed in any of claims 8 to 14 which contains 0.1 to 0.5% by weight of thiocarbamide derivative, 1 to 2% by weight of reducing agent and 0.1 to 0.5% by weight of organic chelating agent. 115

16. A composition as claimed in claim 8 substantially as hereinbefore described with reference to any of the foregoing Examples.

5 17. A process as claimed in claim 1 substantially as hereinbefore described with reference to any of the foregoing Examples.

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